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Shape control of nickel nanostructures incorporated in amorphous carbon films: From globular nanoparticles toward aligned nanowires

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The growth of nickel/carbon nanocomposite thin films by a hybrid plasma process, which combines magnetron sputtering and plasma enhanced chemical vapor deposition, has been investigated. This study has shown that the films consist of nickel-rich nanostructures embedded in an amorphous carbon matrix. The size, the distribution, the density, and the shape of these nanostructures are directly dependent to the total carbon content within the films. At low carbon content (~ 28 at. %), dense nanowire array perpendicularly oriented to the surface of the substrate can be fabricated. For an intermediate carbon concentration (~ 35 at. %), the nickel phase was organized into elongated nanoparticles. These nanoparticles became spherical when reaching a higher carbon content (~ 54 at. %). The extensive structural study allowed the representation of a structure zone diagram, as well as, the development of a scenario describing the growth mechanisms that take place during the deposition of such nanocomposite material. © 2012 American Institute of Physics.

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I. INTRODUCTION

Metal/carbon nanocomposites (nc-Me/C) thin films were proposed in the eighties by Dimigen *et al.* as multifunctional hard coatings.¹ Such a nanocomposite can be described as a heterogeneous material which is formed of two different phases. The first phase represents the highly conductive metal carbide nanoparticles which are randomly distributed in an insulating amorphous carbon phase acting as a matrix (Fig. 1). The association of these two phases gave birth to a new class of material (e.g., nanocomposite) which provides several original and adjustable properties which are not present for its individual constituents.

Since the work reported by Dimigen *et al.*, the research topic of nc-Me/C thin films has attracted an impressive attention from both the scientific and industrial communities. The interest of these two different communities in regard to this material allowed, over the years, the construction of a huge package of scientific data for different Me/C systems. The used metals can be classified into three different categories:

- (i) Metals with high affinity to carbon such as tungsten^{1–4} and titanium.^{5–21} These metals are able to form a hard and thermodynamically stable metal carbide compounds. The nc-Me/C films based on metals of this category are in general considered as good candidates for protective coating applications.^{2,3,7–16}
- (ii) Metals with low affinity to carbon such as cobalt^{22–32} and nickel.^{33–49} Such ferromagnetic metals can form a soft and thermodynamically unstable metal carbide

compounds. The nc-Me/C films based on such metals are in most of cases considered for studies due to the special magnetic properties of the ferromagnetic metals which make of this films suitable candidates for magnetic recording media applications.^{22–24,29,33,36,44}

In addition to their interesting magnetic behavior, several recent studies have demonstrated that this class of materials is quite interesting for the development of piezoresistive devices such as strain-gauge.^{40,41}

- (iii) Metals non miscible with carbon such as platinum,^{43,50} gold,⁵⁰ and copper.^{30,31,51–53} Few studies have been dedicated for the development of applications based on such nanocomposites.^{51,52}

The microstructure of the nc-Me/C films can be mainly represented by the size and the shape of the nanoparticles, the mean grain separation (e.g., the average thickness of carbon separating the nanoparticles), as well as the type of the carbon matrix (e.g., diamond-like carbon, polymer-like carbon, etc.).^{7,10,12,21} It has been made clear that these parameters have a direct impact on the properties of the nanocomposite material.^{32,33,39,44,47,48} Therefore, the accurate control of the microstructure is one of the main issues allowing the preparation of a material with adequate properties for a specific application. Understanding the growth mechanisms of the films should lead to a better control of the microstructure. First, an extensive knowledge of the microstructure is required to construct a scenario describing the growth mechanisms. In the case of nc-Ni/C, as recently pointed by Abrasonis *et al.*,³⁷ the formation of nickel nanoparticles embedded in an amorphous carbon matrix can be explained according to the structure zone model proposed for nanocomposite thin films.^{54,55} It has also been reported that the growth mechanisms in nc-Ni/C films,

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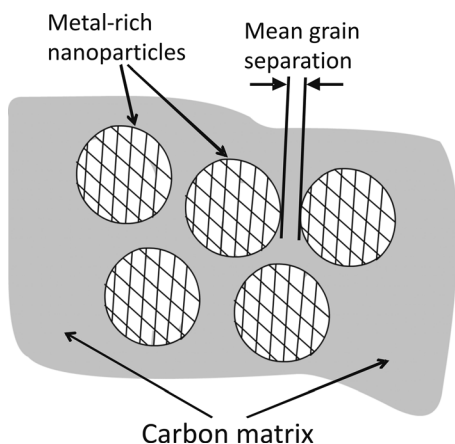


FIG. 1. Schematic illustration of the structure of metal/carbon nanocomposite material.

grown at low temperature by physical vapor deposition (PVD), arise from a several competitive kinetic factors such as the growth rate, surface diffusivity of the adatoms, energy of the incoming ions, ballistic atomic displacements produced by the ion bombardment during the growth, and coalescence of the metal-rich nanoparticles.^{37,42} However, since these parameters vary from a deposition technique to another, the growth mechanisms of such material can be altered and, therefore, the structure of the films grown by two different techniques may not be the same.

In a previous work, we have demonstrated the possibility of synthesizing nc-Ti/C material by an original hybrid plasma process which combines magnetron sputtering of a titanium target and plasma enhanced chemical vapor deposition using methane as a precursor for the deposition of hydrogenated carbon.^{56,57} Recently, we have also reported on the growth of continuous nickel nanowires in amorphous carbon films using this hybrid process, but our study was mainly devoted to the annealing effect of such films.⁴⁹ Therefore, no explanation was provided concerning the formation of such a nanocomposite when using this hybrid process. The focus of this article is on the growth mechanisms taking place in nc-Ni/C films prepared by the same hybrid plasma process that we have employed in our previous works. A systematic structural study will be performed for an extended range of film composition with a carbon content which varies between 5 at. % and 70 at. %. Based on the observed microstructures, a structure zone diagram describing the microstructural evolution will be built-up, and a scenario describing the growth mechanisms of the nanocomposite films will be constructed.

II. EXPERIMENT

A. PVD/PECVD apparatus

The nc-Ni/C films were deposited using a hybrid physical vapor deposition/plasma enhanced chemical vapor deposition (PVD/PECVD) system (Fig. 2). A radio frequency (rf) generator operating at 13.56 MHz was connected to a balanced magnetron sputtering source via a matching box. A nickel disk (99.999% pure and 50 mm in diameter) was used as a target. The distance between the target and the substrate was

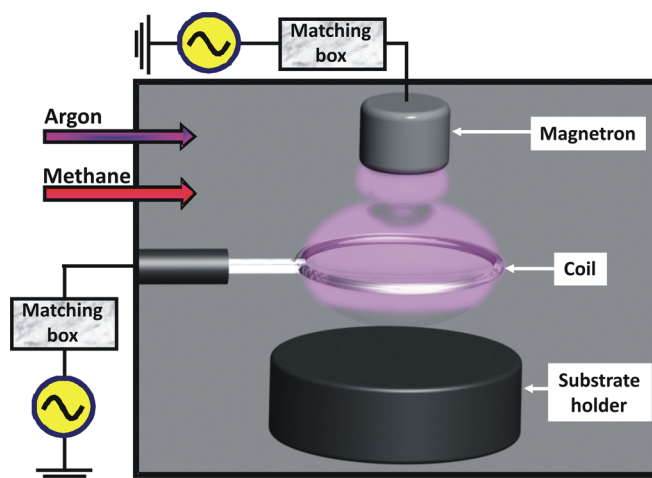


FIG. 2. Sketch of the experimental-setup employed for the growth of nc-Ni/C films.

80 mm. Another rf generator was connected through a matching box to a one turn stainless steel coil, located at an equal distance from the target and the substrate, to generate an additional plasma. In a pure argon atmosphere, the reactor is operated in PVD mode and, therefore, pure nickel can be sputtered and deposited. The addition of a flow of CH₄ gas leads to the deposition of hydrocarbon species by PECVD. Thus, when the reactor is operated in PVD/PECVD mode, a simultaneous deposition of metal and carbon takes place leading to the formation of nc-Ni/C films. By adjusting the methane fraction in the plasma during the deposition, the carbon concentration present in the films can be controlled. The methane fraction can be defined using the following equation:

$$\text{Methane fraction} = \frac{\phi_{\text{CH}_4}}{\phi_{\text{CH}_4} + \phi_{\text{Ar}}} \times 100, \quad (1)$$

where ϕ_{CH_4} and ϕ_{Ar} represent the methane and argon flows, respectively.

B. Deposition conditions

During deposition, the rf powers coupled to the coil and to the magnetron were both fixed at 150 W. The pressure during the deposition was maintained at 0.67 Pa. The substrate was at floating potential and no substrate heating was applied. In these conditions, the potential difference between the plasma and the substrate is evaluated at about 26 V.⁵⁶ The total gas flow of the injected argon and methane gas into the deposition chamber was fixed at 12 sccm. In order to modify the carbon content within the films, the methane fraction injected into the deposition chamber has been varied.

C. Material characterization

The surface chemical state of the films has been investigated by *ex situ* x-ray photoelectron spectroscopy (XPS) using a Kratos Axis Ultra spectrometer and monochromatic Al K α radiation (1486.6 eV). Before analysis, the surface contamination layer was removed by 10 min of Ar⁺ sputtering in the XPS system under ultra high vacuum. The ion

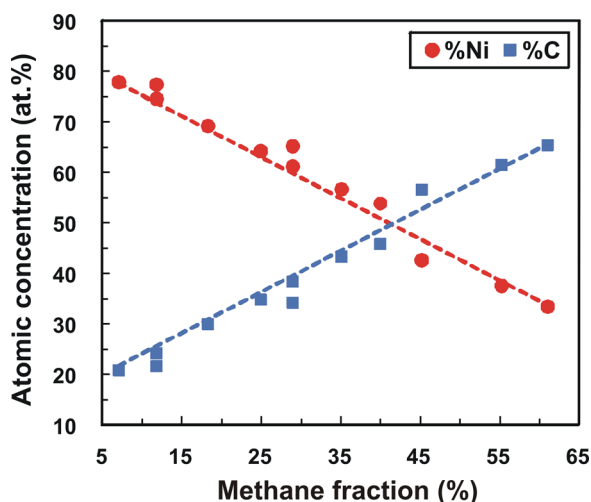


FIG. 3. Evolution of the nickel and carbon content within the nc-Ni/C films as a function of the methane fraction in the plasma.

energy during the cleaning procedure was fixed to 5 keV, whereas the ion current measured on the sample was 2 μ A. For the chemical study of C 1s and Ni 2p, XPS regions were acquired at a 20 eV pass energy leading to an energy resolution of approximately 0.48 eV. Scanning electron microscopy (SEM) imaging was performed at 5 kV on a JEOL JSM 7600F microscope. The crystalline phases present in the samples were probed by x-ray diffraction (XRD) which was carried out on a Siemens D5000 x-ray diffractometer in Bragg–Brentano $\theta/2\theta$ geometry using the Cu K α radiation. Transmission electron microscopy (TEM) imaging was performed on a Hitachi H-9000 NAR microscope (LaB₆ filament, 300 kV, Scherzer resolution: 0.18 nm). For cross-sectional TEM analysis, the specimens were prepared by mechanical polishing followed by ion milling. In case of plan view analysis, a film was directly deposited during 2 min on a TEM grid covered with a thin holey layer of carbon.

III. RESULTS AND DISCUSSION

A. Chemical bonding

The Ni 2p and C 1s XPS spectra were used in order to determine the surface chemical composition of the nc-Ni/C films (Fig. 3). It was found that increasing the methane frac-

tion in the plasma induces an increase of the carbon content within the films. This result, which is in good agreement with our previous study on nc-Ti/C films,⁵⁷ demonstrates the ability of this hybrid process to easily control the chemical composition of the films in a wide range while maintaining the stability of the plasma discharge. As shown in Fig. 4(a), the Ni 2p spectra of all the samples were similar and they exhibit two main components located at 853 eV (Ni1) and 870.5 eV (Ni2). They can be attributed to the core levels 2p_{3/2} and 2p_{1/2}, respectively, and are characteristics of metallic nickel and/or conductive nickel compounds.^{34,38,58} In addition, they exhibit satellites at 859.5 eV (Ni1*) and 876 eV (Ni2*). Compared to pure fcc nickel, the positions of these peaks are shifted by ~ 1 eV toward higher binding energies reflecting the carbide state of nickel.³⁶ For the C 1s spectra, three components can be observed (Fig. 4(a)). The first one located at 283.5 eV (labelled C1) can be attributed to the carbon atoms bonded to the nickel ones (Ni-C) present in a sub-stoichiometric Ni₃C phase,^{59–62} which is called NiC_x (with $x \leq 0.33$). The second component at 284.5 eV (labelled C2) can be attributed to the carbon atoms present in an amorphous carbon phase.^{34,38,62} The origin of the third component C3 at about 286 eV is not well understood. Some authors attribute this component to the presence of sp³ hybridized carbon atoms present in an amorphous hydrogenated carbon phase.^{63,64} The evolution of the relative intensities of these components as a function of the carbon content are plotted in Fig. 4(b). Increasing the carbon content within the film leads to a decrease of the relative intensity of C1 (Ni-C) and to an increase of the intensity of C2 (C-C). The evolution of the relative intensities of these components leads to the following conclusion: when increasing the carbon content within the films, the relative amount of nickel carbide decreases, whereas the one of amorphous carbon increases.

B. Morphology and microstructure

1. SEM

An evolution of the morphology of the films can be seen when increasing the carbon content in the films (Fig. 5). For a low carbon concentration, the films have a columnar morphology as displayed in Fig. 5(a). When increasing the carbon content up to 28 at. %, the morphology of the films becomes fibrous (Fig. 5(b)), and it can be remarked that the

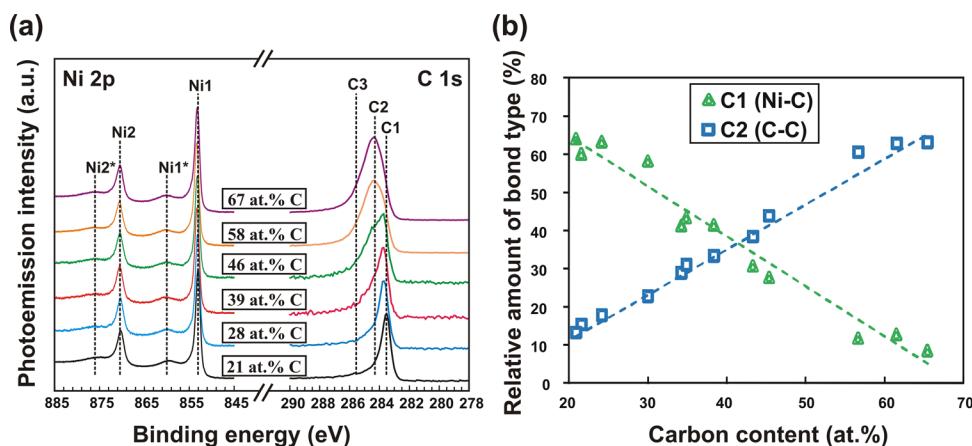


FIG. 4. Ni 2p and C 1s XPS spectra of the prepared nc-Ni/C thin films (a). Evolution of the relative amount of the different chemical environments, deduced from C 1s XPS spectra, as a function of carbon content (b). The dashed lines shown on (b) are only used as guides for the eyes.

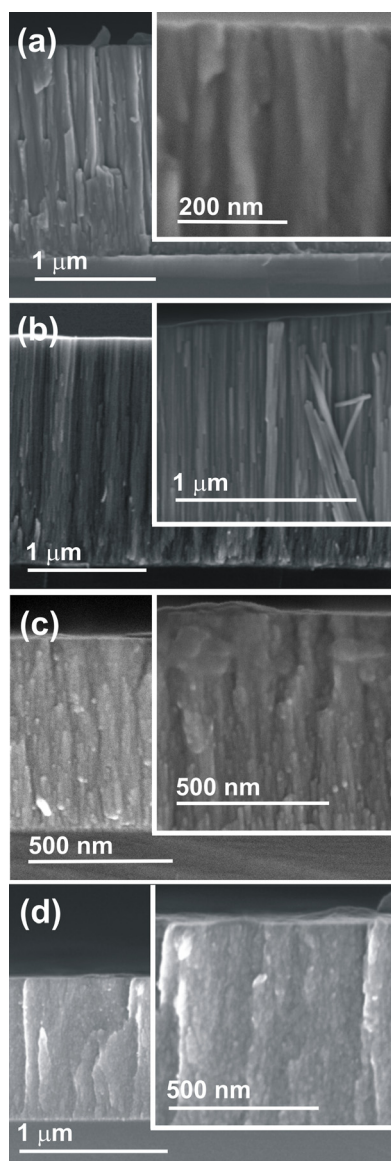


FIG. 5. Cross-sectional SEM images of nc-Ni/C films with various carbon content: 21 at. % (a) 28 at. % (b) 35 at. % (c), and 46 at. % (d).

film is formed of a dense array of aligned nanowires. When the carbon content reaches 35 at. %, the fibrous structure observed previously disappears and a granular morphology can be seen (Fig. 5(c)). For a higher carbon concentration (~46 at. %), the morphology of the films stays globular (Fig. 5(d)). The size of the observed grains cannot be evaluated from the SEM image due to the limited resolution of the used microscope.

2. XRD

In order to illustrate the evolution of the crystalline structure, a selection of XRD patterns recorded at different carbon contents is presented in Fig. 6. The diffraction peaks detected for a sample with 5 at. % of carbon indicate the presence of fcc nickel. Indeed, we observe two peaks at 44.4° and 51.7° which can be attributed to the lattice planes (1 1 1) and (2 0 0) of fcc nickel, respectively. For such film, the incorporation of carbon atoms in the fcc nickel lead to a distortion in its lattice

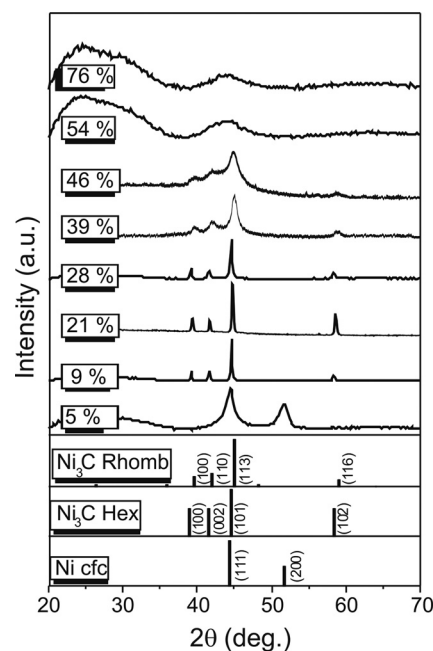


FIG. 6. XRD patterns recorded for nc-Ni/C films grown with different carbon content.

parameter resulting in a broadening of the diffraction peaks. With increasing the carbon content within the films, new diffraction peaks appear (positions around: 39.2° , 41.6° , 58.5° , 71.1° and 78.0°), while the peak at 51.7° ((200) of fcc nickel) is no longer present. This result indicates a modification of the crystalline structure of the films. The new diffraction peaks can be attributed to nickel carbide (Ni_3C) phase.³⁵ When reaching 54 at. % of carbon, the diffraction peaks become very broad indicating the amorphous state of the films or the very small size of the crystalline nanoparticles.

3. TEM

As shown in the TEM plan-view micrographs presented in Fig. 7, a clear modification of the microstructure occurs when modifying the chemical composition of the films. At low carbon content (21 at. %), the obtained structure looks similar to the one of pure nickel (not presented here) (Fig. 7(a)). When increasing the carbon content up to 28 at. %, a phase separation between the nickel and carbon occurs (Fig. 7(b)). In this case, the nickel carbide phase gets organized in a circular shape (dark disks) which is surrounded by the amorphous carbon phase (thin bright layers). At 39 at. %, the mean diameter of the dark disks, representing the nickel carbide phase, becomes smaller (Fig. 7(c)). Between 46 at. % and 67 at. %, the mean diameter of the nickel-rich disks takes its lowest value ~ 3 nm (Figs. 7(d)–7(f)).

In order to construct a 3D schematic representation of the observed nanostructures, a cross-sectional TEM analysis has been performed. Three different conditions (carbon concentration: 28 at. %, 35 at. %, and 54 at. %) were selected (Fig. 8). The structure of the nc-Ni/C film with 28 at. % of carbon consists of vertically oriented nickel carbide nanowires which are encapsulated in an amorphous carbon matrix (Fig. 8(a)). At 35 at. % of carbon, the nanowires observed

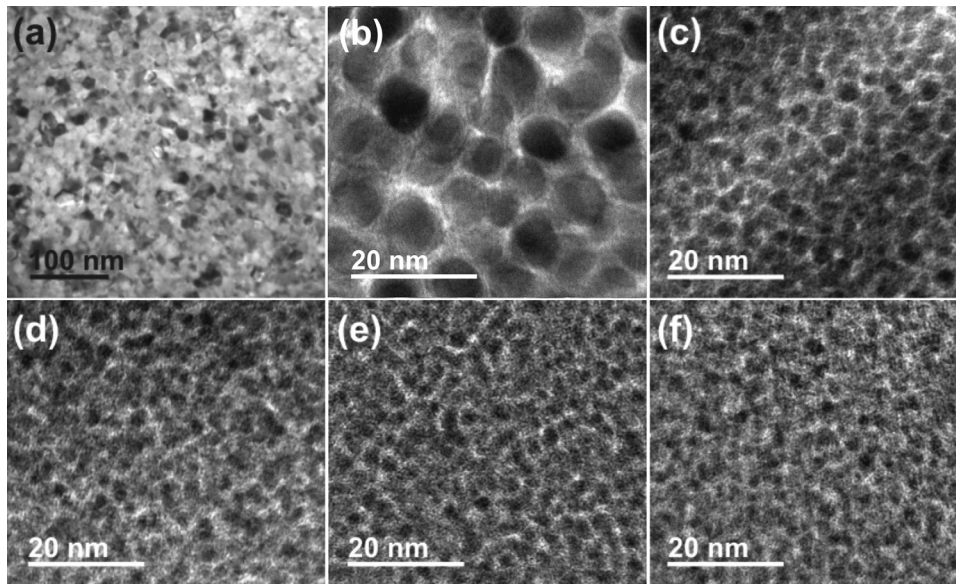


FIG. 7. Plan-view TEM micrographs recorded for nc-Ni/C films with various carbon content: 21 at. % (a) 28 at. % (b) 39 at. % (c) 46 at. % (d) 58 at. % (e), and 67 at. % (f).

previously become shorter (Fig. 8(b)); in other words, the nickel carbide phase at this stage consists of elongated nanoparticles. Furthermore, when increasing the carbon content up to 54 at. %, the nanoparticles becomes spherical with mean diameter of 4 nm (Figs. 8(c) and 8(d)).

C. Grain size

In general, the size of the metal nanoparticles incorporated in the nc-Me/C is an essential parameter to understand the properties of the films.^{7,9-13,28} For this reason, the evolution of this parameter as a function of carbon content within the films has been considered for study. As we have seen previously, the TEM analysis has revealed two characteristic dimensions for the nickel carbide nanoparticles:

- (i) The first dimension, demonstrated by plan-view TEM imaging, represents their lateral size D that can be measured along the axis parallel to the surface of the substrate.
- (ii) The second dimension, demonstrated by cross-sectional TEM imaging, represents the height H measured along the growth direction of the films (e.g. direction perpendicular to the surface of the substrate).

If the aspect-ratio H/D is higher than 1 (Fig. 9(a)–left), the nanoparticle exhibits an elongated shape along the growth direction; whereas when H/D tends to 1 (Fig. 9(a)–right), the shape of the nanoparticles becomes spherical. The first dimension H can be determined by applying the Scherrer formula to the most intense peak of the XRD patterns (position $\sim 44.5^\circ$), whereas D can be directly evaluated from the TEM plan-view micrographs. It should be noticed that D has been only measured for the samples where the formation of nanocomposite was demonstrated by TEM (e.g., no measurements were done between 5 at. % and 21 at. % of carbon).

The values of H and D are plotted in Fig. 9(b) as a function of the total carbon content within the films. It can be seen that the value of H raises from 6 nm to 32 nm when increasing the carbon content from 5 at. % to 9 at. %. This can be simply explained by the fact that at 5 at. % of carbon, a fcc nickel phase with a poor crystalline structure can be obtained, whereas at 10 at. % of carbon a nickel carbide phase with an enhanced crystalline structure is formed (see Sec. III B 2). Moreover, when further increasing the carbon concentration within the films, the value of H decreases sharply till reaching 3 nm at 54 at. % of carbon. A similar evolution has been observed for the lateral size D which decreases when increasing the carbon concentration. Moreover, when reaching 42 at. % of carbon, the lateral size D becomes almost constant. Meanwhile, when comparing the evolution of these two parameters, it can be remarked that at low carbon content (~ 28 at. % of carbon), the vertical size H is higher than the lateral size D (e.g., aspect ratio $H/D \sim 2.7$). This result reveals the presence of a shape-anisotropy which has been previously observed on the cross-sectional TEM

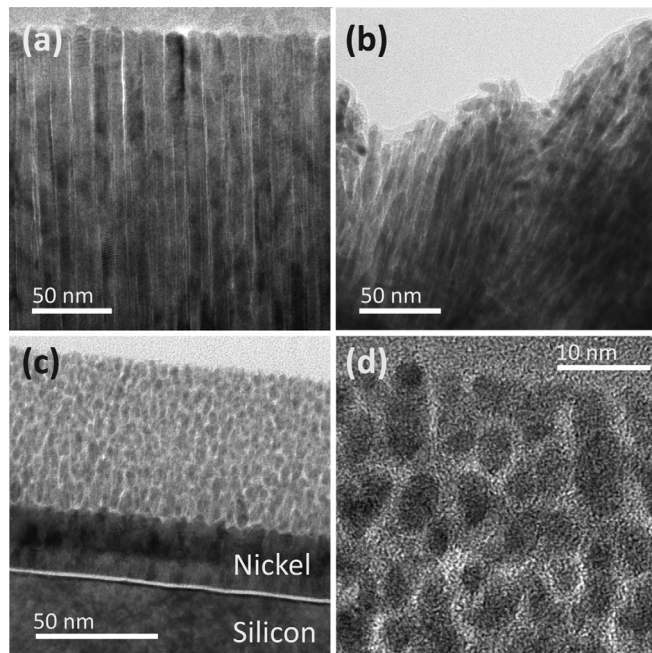


FIG. 8. Cross-sectional TEM micrographs of nc-Ni/C films synthesized with different carbon concentration: 28 at. % (a), 35 at. % (b), and 54 at. % (c) and (d).

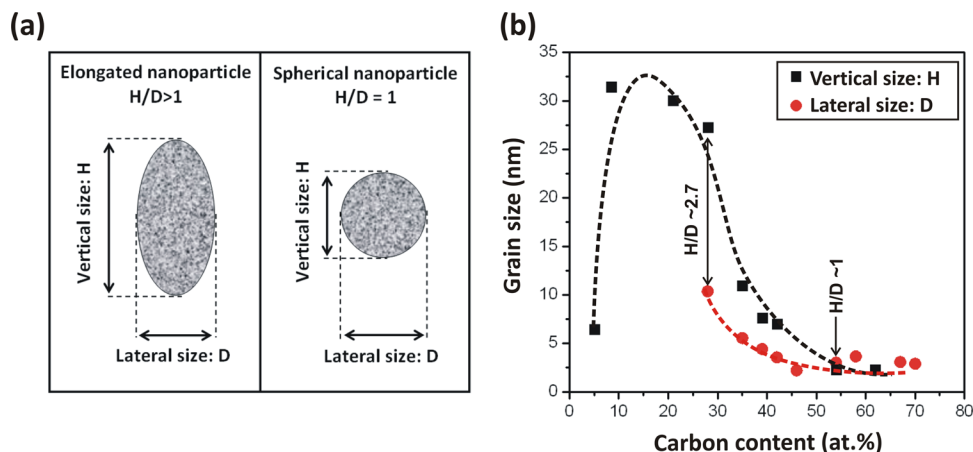


FIG. 9. Schematic of elongated and spherical nanoparticles showing the vertical H and the lateral size D which define their shape (a). Evolution of the vertical H and the lateral sizes D of nanoparticles as a function of the carbon content within the films (b). The vertical size of the particle H can be determined by applying the Scherrer formula to the XRD patterns, whereas the lateral size D can be determined from the TEM plan-view micrographs. The parameter H/D indicated on (b) represents the aspect-ratio of the nanoparticle.

images (see Fig. 8). It can be also seen that when reaching 54 at. % of carbon, H becomes approximately equal to D (e.g., aspect ratio $H/D \sim 1$).

D. Mean grain separation

The mean grain separation S is another parameter playing a main role on the properties of the nc-Me/C films.^{7,10,12,21} The mean grain separation S can be defined as the thickness of the amorphous carbon matrix separating the crystalline nanoparticles from each other. This parameter is in general very small and only TEM analysis can reveal its presence (Fig. 10). However, the measurement of the mean grain separation using TEM would not be reliable for the following reasons:

- The mean grain separation S can be measured only when the nanoparticles are very well defined and separated from each other (Fig. 10(a)).
- Since the TEM analysis delivers a 2D image of the bulk of the film, the superposition of different nanoparticles present in the bulk of the film can give the impression of the presence of agglomerated (Fig. 10(b)) or percolated (Fig. 10(c)) nanoparticles. In case of superposition, agglomeration, or percolation, the mean grain separation cannot be picked-up from the TEM images.

The mean grain separation can be estimated by using a simple geometrical representation (Fig. 11) combined with

experimental data: phase composition determined by XPS and grain size of the nickel carbide nanoparticles. The fact that XPS is a surface analysis technique and not a bulk one should be taken into account in this geometrical representation. Therefore, we consider that the analyzed surface of the nickel carbide nanoparticles has a shape of hexagons of uniform size which are distributed along a 2D hexagonal lattice system (Fig. 11). The lateral dimension of a hexagon is considered equal to the lateral grain size D deduced previously by TEM measurements. The distance separating the hexagons, which is filled by amorphous carbon, represents the mean grain separation S .

Let us consider a unit cell of this 2D hexagonal lattice system (highlighted in red on Fig. 11). The parameter $[Ni]$, deduced from XPS, represents the atomic concentration of nickel in the nickel carbide phase of the unit cell. It is proportional to the density of nickel atoms in the nickel carbide phase n_{Ni} , as well as to the surface occupied by this carbide phase in a unit cell:

$$[Ni] \propto \frac{\sqrt{3}}{2} n_{Ni} D^2. \quad (2)$$

We can define the parameter $[C_{a-C}]$ as the atomic concentration of carbon in the amorphous carbon phase of a unit cell. This quantity is proportional to the density of the carbon atoms n_{a-C} in the amorphous carbon phase, as well as to the surface occupied by the amorphous carbon in a unit cell:

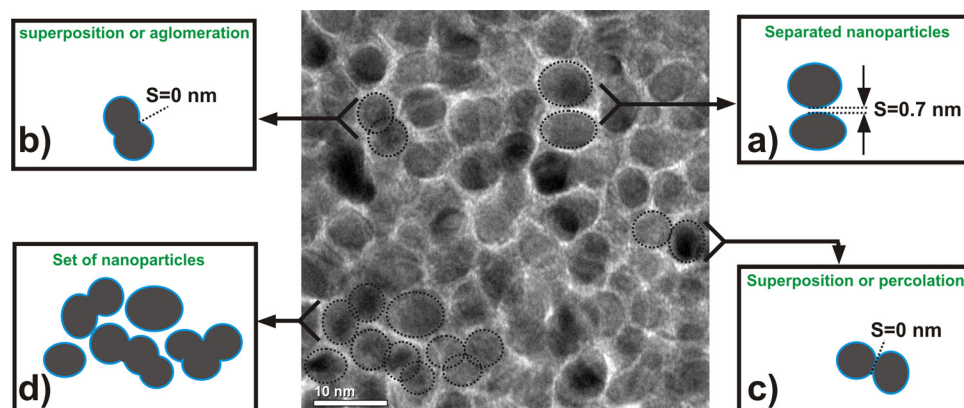


FIG. 10. An example of processing a plan-view TEM micrograph of nc-Ni/C film grown at 28 at. % of carbon. Separated nanoparticles (a), superposed or agglomerated nanoparticles (b), superposed or percolated nanoparticles (c), and a set of nanoparticles (d).

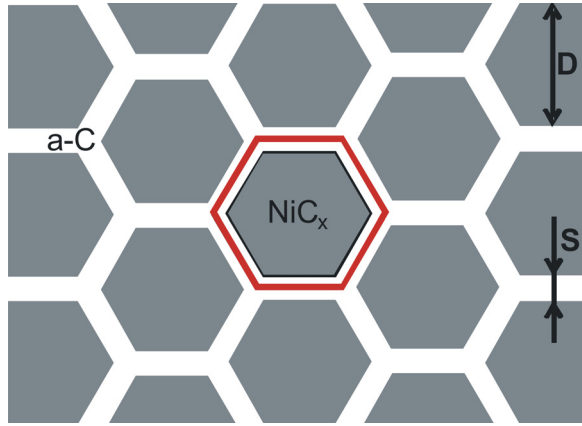


FIG. 11. Sketch of a simple geometrical representation used to estimate the mean grain separation S . The hexagons in gray represent the surface of the nanoparticles analyzed by XPS, whereas the white regions represent the amorphous carbon matrix. The lattice cell of this 2D hexagonal system is illustrated in red.

$$[C_{a-C}] \propto n_{a-C} \frac{\sqrt{3}}{2} ((S+D)^2 - D^2). \quad (3)$$

This parameter $[C_{a-C}]$ can be calculated using the total atomic concentration of carbon $[C]$ in the films deduced from XPS and by taking into account the fraction $[C_1]$ of carbon atoms in the NiC_x phase:

$$[C_{a-C}] = (1 - [C_1])[C]. \quad (4)$$

From Eqs. (2)–(4), the composition of the films deduced from XPS can, therefore, be related to the mean grain separation S :

$$\frac{[C_{a-C}]}{[Ni]} = \frac{(1 - [C_1])[C]}{[Ni]} = \frac{((D+S)^2 - D^2)n_{a-C}}{D^2 n_{Ni}}. \quad (5)$$

The expression of S can be deduced from Eq. (5):

$$S = D \left[\sqrt{\left(1 + \frac{n_{Ni}}{n_{a-C}} \left(\frac{(1 - [C_1])[C]}{[Ni]} \right)\right)} - 1 \right]. \quad (6)$$

Taking into account the carbide state of the nickel nanoparticles, the ratio $\frac{n_{Ni}}{n_{a-C}}$ can be written as follows:

$$\frac{n_{Ni}}{n_{a-C}} = \frac{1}{\left(1 + \left([C_1] \frac{[C]}{[Ni]}\right)\right)} \frac{\rho_{Ni}}{\rho_{a-C}} \times \frac{M_C}{M_{Ni}}. \quad (7)$$

In this expression, M_C stands for the atomic weight of carbon taken equal to 12.0 amu, M_{Ni} for the atomic weight of nickel (~ 58.7 amu), ρ_{Ni} is the density of nickel taken equal to 8.9 g.cm^{-3} , and ρ_{a-C} represents the density of carbon. For hydrogenated amorphous carbon films, the typical value of ρ_{a-C} range between 1.6 and 2.5 g.cm^{-3} .

Finally, by replacing Eq. (7) in Eq. (6), the general expression of S can be written as follows:

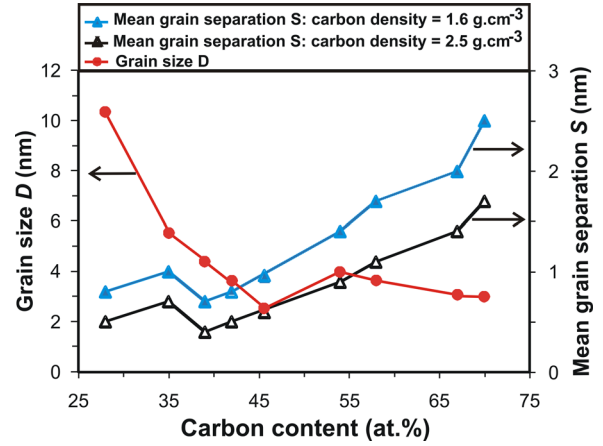


FIG. 12. Evolution of the mean grain separation S and the lateral grain size D as a function of the total carbon content within the films. Two different values of amorphous carbon density have been used to determine S : 1.6 g.cm^{-3} (blue curve) and 2.5 g.cm^{-3} (black curve). The solid lines are only used as guides for the eyes.

$$S = D \left[\sqrt{\left(1 + \frac{(1 - [C_1])[C]}{([Ni] + [C_1][C])} \times \frac{\rho_{Ni}}{\rho_{a-C}} \times \frac{M_C}{M_{Ni}}\right)} - 1 \right]. \quad (8)$$

The calculated values for the mean grain separation using Eq. (8) are plotted in Fig. 12 as a function of carbon content for two estimated values of ρ_{a-C} (1.6 and 2.5 g.cm^{-3}). The uncertainty introduced by ρ_{a-C} leads to a maximal error of about ± 0.4 nm for the estimated value of S . The mean grain separation remains lower than 1 nm and is almost constant for carbon content lower than 45 at. %. A slight increase is observed for higher carbon contents. At 70 at. %, S is in the 2 nm range.

E. Growth mechanisms

The results provided from the structural and the morphological studies presented previously can be resumed in the structure zone diagram shown in Fig. 13. Four zones can be identified. The first zone includes the homogenous films with a columnar structure of nickel or nickel carbide. In this zone, no nanocomposite was formed. In the second zone, the films have a fibrous structure, and they consist of nickel carbide nanowires with a high aspect ratio which are wrapped by an

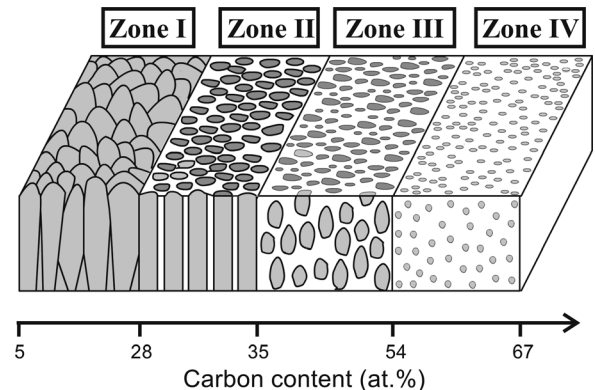


FIG. 13. Structure zone diagram describing the structural evolution of the nc-Ni/C films as a function of carbon concentration.

amorphous carbon matrix. The third and the fourth zones represent the nc-Ni/C films which consist, respectively, of elongated and spherical nanoparticles which are randomly distributed in the amorphous carbon matrix. The presence of four different types of film structure can be related to the growth mechanisms that take place in such films which vary from one zone to another.

In Zone I, the observed columnar structure can be explained by the classical growth mechanisms in thin films of elementary material deposited by PVD at low pressure and low temperature.⁵⁵ The structure corresponding to Zone II has been reported in literature for nanocomposite material based on various systems such as Co/C,^{25,28} metal/silicon,^{65–67} and metal/germanium.⁶⁷ Several theoretical studies were devoted to understand the growth mechanisms leading to the formation of such a structure with a cylindrical geometry in multiphase systems.^{68–71} An analogy between

Ni/C and these multiphase systems can be established in order to construct a scenario explaining the driving forces leading to the formation of such cylindrical structures in our study. The different stages of the growth of nc-Ni/C films in Zone II are sketched in Fig. 14(a). Knowing the chemical composition of the deposited films, we can conclude that in this zone, the flux of the deposited nickel atoms is much higher than the one of carbon. As the films are grown at low temperature, therefore, the bulk diffusion can be neglected and only surface diffusion can take place.³⁷ This effect is known as the frozen bulk approximation.^{68,71} In the early stage of growth, the nickel and carbon adatoms diffuse on the surface of the substrate. The surface diffusion length, L_{dif} , of these adatoms is limited by the covering rate due to deposition.^{69,71} It can be expressed by the following equation:

$$L_{dif} = \sqrt{D_{dif}\tau_{ML}}, \quad (9)$$

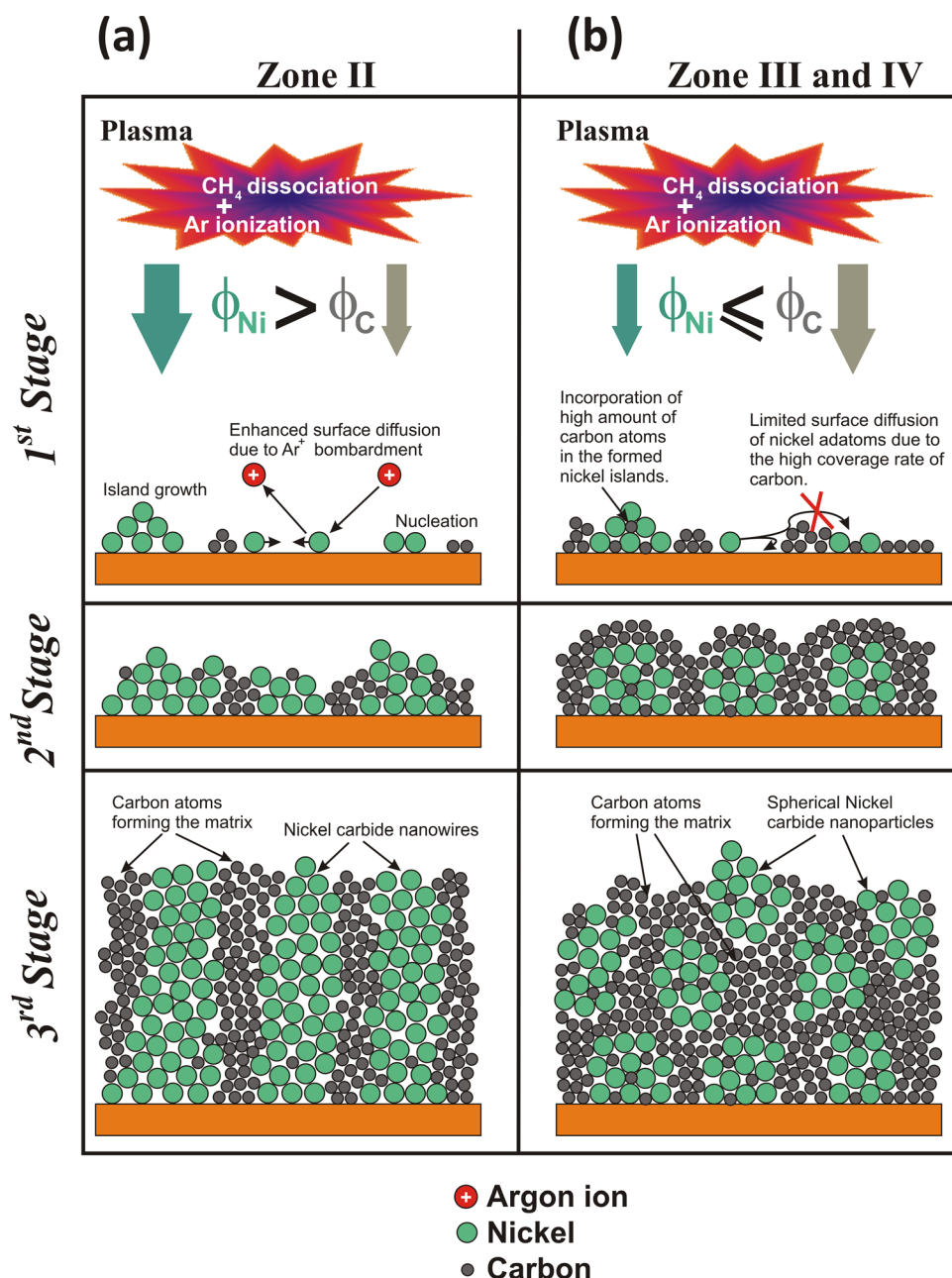


FIG. 14. Different stages of the scenario used to explain the growth mechanisms in nc-Ni/C films leading to the formation of nickel carbide nanowires (a) or spherical nanoparticles (b).

where D_{dif} in this equation stands for the surface diffusion coefficient which can be enhanced due to the argon ions bombardment generated by the plasma during the growth.^{20,71,72} The parameter τ_{ML} is the deposition time of one monolayer.

Due to the low miscibility of nickel with carbon, these two different species, favoring phase separation, separate and condense on the surface of the substrate in order to reduce the total free energy. Since in this zone II, the flux of the deposited nickel atoms is much higher than the one of carbon, the development of the nickel islands will be dominant. That is why the nickel domains occupy the majority of the surface and become wrapped by the amorphous carbon phase. As a consequence, the formation of a carbon phase between the nickel islands will block the lateral development (e.g., parallel to the surface of the substrate) of these metal islands, and, therefore, their growth will continue preferentially along the growth direction (e.g., direction perpendicular to the surface of the substrate). Very low amount of carbon atoms can get incorporated in the nickel islands leading to the formation of a sub-stoichiometric nickel carbide phase. Moreover, as the deposited nickel atoms continuously reach the surface, they will diffuse as far as they randomly join a nickel island formed at the early stage of the growth. On the other hand, the carbon ad-atoms will diffuse on the surface favoring to chemically get bonded to the carbon phase initially filling the spaces between the nickel islands. If the vertical development of the nickel islands is not intercepted by at least one continuous monolayer of carbon, they will keep getting vertically expanded as a function of the deposition time until forming nickel carbide nanowires wrapped by amorphous carbon. In this case, the length of the formed cylindrical nanowires, which can be related to the deposition time, is equal to the thickness of the film (Fig. 14(a)). The diameter of the nanowires is determined by the value of the surface diffusion length L_{dif} of the nickel ad-atoms for the selected deposition condition.⁷¹

In zone III and zone IV, repeated nucleation events occurs leading to the formation of a multiphase structure with the occurrence of discrete elongated or spherical nanoparticles surrounded by a bright layer of amorphous carbon. The reasons for the repeated nucleation are not well understood as many processes can lead to such behavior.^{38,55} In our case, such type of multiphase structure is observed when increasing the methane fraction in the plasma and reducing the one of argon. When doing so, the flux of the deposited carbon atoms increases and it becomes comparable to the one of nickel (Fig. 14(b)). There are two main consequences for this modification:

- (i) When the argon flux gets reduced, the argon ion bombardment during the growth of the films will decrease. As a result, the diffusion coefficient D_{dif} diminishes leading to the decrease of the surface diffusion length L_{dif} . In addition, the increase in flux of the deposited carbon atoms will enhance the coverage rate of carbon. As a result, the nickel ad-atoms will not be able to diffuse sufficiently fast to reach the existing clusters before these last become masked by amorphous carbon (Fig. 14(b)). Therefore, the lateral size of the

nickel nanoparticles shrink as it was shown previously in the plan-view TEM micrographs (see Fig. (7)).

- (ii) In such conditions, the probability of covering the metal clusters by carbon will raise.¹⁰ If carbon does not diffuse sufficiently fast on Ni, the carbon ad-atoms will nucleate on the nickel clusters and quench their vertical growth (Fig. 14(b)—2nd stage).³⁸ As a consequence, a new nickel clusters must nucleate somewhere else and grow until they get masked by carbon (Fig. 14(b)—3rd stage).

Thus, the modulation of the nickel carbide nanostructures arises from a competition between the phase separation and the continuous deposition of material on the surface. If the vertical development of the nickel-rich domains is kinetically a little bit faster than the coverage rate of carbon, thus, elongated nickel-rich nanoparticles will be obtained as illustrated in Zone III of the structure zone diagram. Whereas, in case where their vertical growth is quite low compared to the coverage rate of carbon, the shape of the nickel-rich nanostructures becomes spherical as illustrated in Zone IV.

IV. CONCLUSION

Nanocomposite nickel/carbon films, composed of nickel carbide nanostructures embedded in an amorphous carbon matrix, have been studied. The films were grown at low temperature by a hybrid plasma process combining magnetron sputtering of a nickel target and deposition of hydrocarbon species by PECVD. By adjusting the methane fraction in the plasma, the chemical composition within the films can be controlled.

In particular, the morphological and structural evolutions of the films as a function of carbon content (5–70 at. %) have been investigated. Thanks to the phase-separation process taking place during the growth, nickel-rich nanostructures with various shapes and distributions within the carbon matrix can be designed. The control of these various parameters makes the employed deposition technique very suitable for the fabrication of ultrahigh-density one-dimensional or globular nickel-rich nanostructures wrapped by amorphous carbon matrix.

In addition to the grain size and the mean grain separation, the shape-anisotropy of the nickel-rich nanostructures that we have demonstrated along this article, which is often missed in different works reported in literature, is a very important parameter that can affects the properties of the films. The mean grain separation was found to be almost constant for low and intermediate carbon content and it slightly increases at high carbon concentration. It should be noted that this parameter may be affected by the deposition conditions (e.g., ion energy, substrate temperature, etc) which vary from a deposition technique to another. Therefore, it is a point of interest to check up this matter for nc-Ni/C films in a further study using the geometrical representation developed in this article.

Understanding the structural evolution of the films helped for the construction of a scenario describing the different growth stages of the nc-Ni/C material. The proposed scenario is expected to be the same for nc-Me/C films, based on metal with low affinity to carbon and deposited by a

similar process. However, a numerical simulation, based on the experimental data found in this work, should be performed in order to clearly understand and describe the growth mechanisms taking place in such material.

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